5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Cresols are widely occurring natural and anthropogenic products. Although cresols appear to be ubiquitous in the environment, their concentrations probably remain low due to their rapid removal rates in most environmental media. In air, cresols probably degrade rapidly because of reactions with photochemically produced hydroxyl radicals. Biodegradation is probably the dominant mechanism responsible for the fast breakdown of cresols in soil and water. Nevertheless, cresols may persist in extremely oligotrophic waters, in those with limited microbial communities, and/or those under anaerobic conditions, such as in some sediments and groundwater aquifers.

High levels of cresol exposure may result from the ingestion of foods containing it. However, more quantitative data on the occurrence of cresols in food are necessary to accurately assess the exposure via the oral route. Based on the available information, the most common route of exposure for the general population is probably inhalation. Cresols are constantly emitted to air via automobile exhaust; consequently, people who live in urban and suburban settings may be constantly exposed to low levels of cresols in the atmosphere. Cresols are also emitted to ambient air during the combustion of coal, wood, and municipal solid waste. Therefore, residents near coal- and petroleum-fueled electricity-generating facilities, municipal solid waste incinerators, and industriei with conventional furnace operations, or largescale incinerators may be exposed to cresols in air. People in residential areas where homes are heated with coal, oil or wood may also be exposed to cresols in air. High levels of cresol exposure can result from active and passive inhalation of cigarette smoke (Wynder 1967)

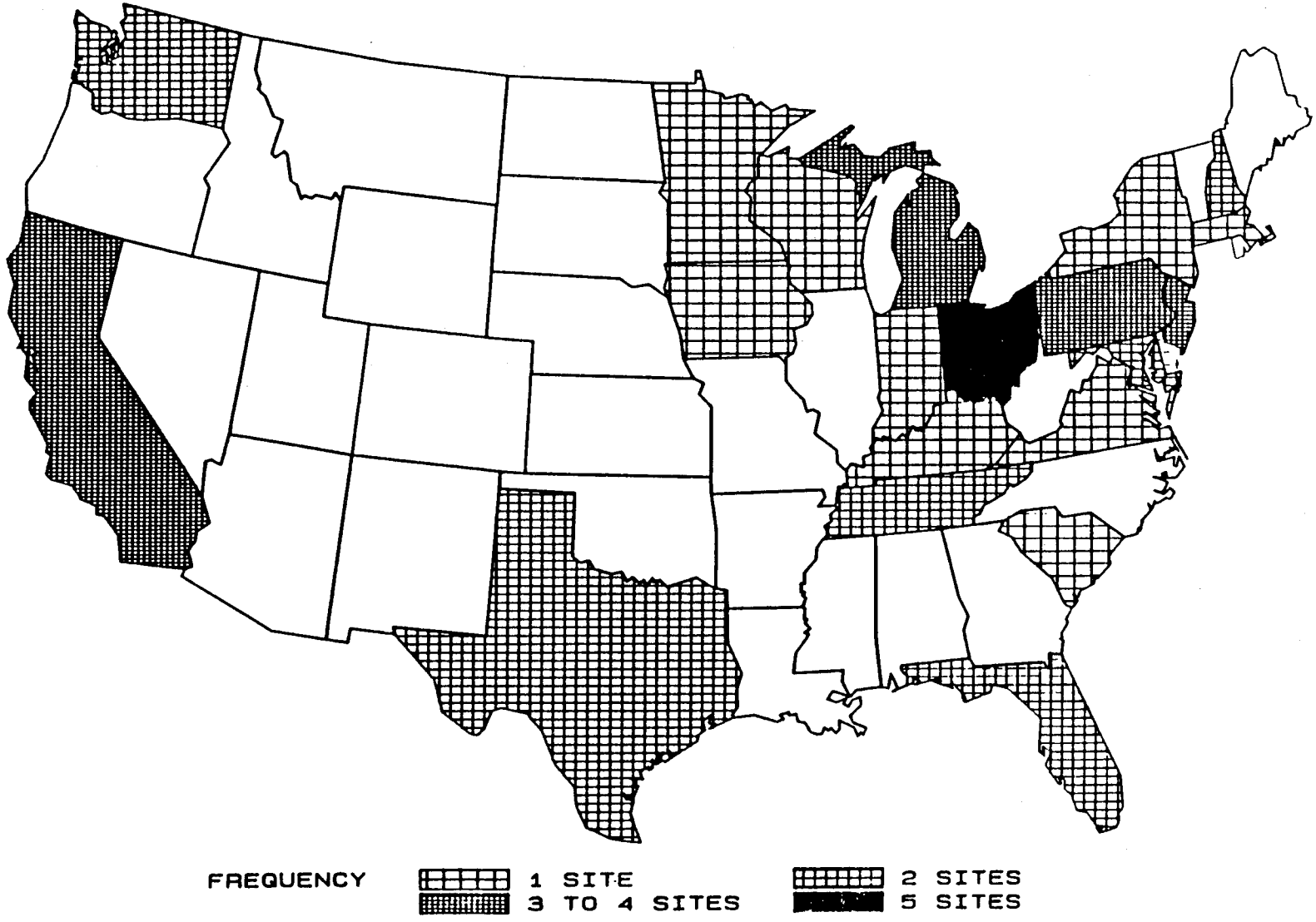
The EPA has identified 1,177 NPL sites. o-Cresol, p-cresol, m-cresol and the mixed isomers have been found at 10, 25, 2, and 12, respectively, of the sites evaluated for these chemicals. However, we do not know how many of the 1,177 NPL sites have been evaluated for these chemicals. As more sites are evaluated by the EPA, these numbers may change (View 1989). The frequency of these sites within the United States can be seen in Figure 5-l.

5.2 RELEASES TO THE ENVIRONMENT

5.2. Air

Cresols are a group of widely distributed natural compounds formed as metabolites of microbial activity and excreted in the urine of mammals (Fiege and Bayer 1987). Cresols occur in various plant lipid constituents, including oils from jasmine, cassia and easter lily, ylang ylang, and Yucca gloriosa flowers, peppermint, eucalyptus, and camphor. Oils from conifers, oaks, and sandalwood trees also contain cresols (Fiege and Bayer 1987). Volatilization

FIGURE 5-1. FREQUENCY OF NPL SITES WITH CRESOLS CONTAMINATION *



* Derived from View 1989

of natural cresols from urine and transpiration of plants may release cresols to the air. Cresols are also a product of combustion and can be released to the atmosphere from natural fires associated with lightning, spontaneous combustion, and volcanic activity (McKnight et al. 1982).

Cresols are natural components of crude oil and coal tar, from which they are recovered as fractional distillates. Cresols are also produced synthetically. The dominant anthropogenic sources for the release of cresols to the atmosphere are fugitive or accidental emissions during the manufacture, use, transport, and storage of cresols or associated products of the coal tar and petroleum industries. Table 5-1 includes information from the Toxic Chemical Release Inventory (TRI 1989) on atmospheric releases of cresols from facilities that process or manufacture cresols. According to the TRI (1989), 140 of 163 facilities that manufacture or process cresols released an estimated 859,600 pounds of this compound to the atmosphere in 1987. The largest single annual air emission was 71,000 pounds. The TRI data should be used with caution since the 1987 data represent first-time reporting by these facilities. Only certain types of facilities were required to report. This is not an exhaustive list.

Low levels of cresols are constantly emitted to the atmosphere in the exhaust from motor vehicle engines using petroleum based-fuels (Hampton et al. 1982; Johnson et al. 1989; Seizinger and Dimitriades 1972). Cresols have been identified in stack emissions from municipal waste incinerators (James et al. 1984; Junk and Ford 1980) and in emissions from the incineration of vegetable materials (Liberti et al. 1983). Cresols have also been identified as a component of fly ash from coal combustion (Junk and Ford 1980). Therefore, coal- and petroleum-fueled electricity-generating facilities are likely to emit cresols to the air. The combustion of wood (Hawthorne et al. 1988, 1989) and cigarettes (Arrendale et al. 1982; Novotny et al. 1982) also emits cresols to the ambient air. Cresols are also formed in the atmosphere as a result of reactions between toluene and photochemically generated hydroxy radicals (Leone et al. 1985).

5.2.2 Water

Cresols are widely distributed natural compounds. As discussed above, they are formed as metabolites of microbial activity and are excreted in the urine of mammals (Fiege and Bayer 1987) and humans (Needham et al. 1984). Cresols from human urine are probably biodegraded at municipal sewage treatment facilities prior to release to ambient waters. However, for combined septic and storm sewage systems, cresols may be released to surface waters during periods of precipitation when influent volumes exceed treatment plant capacities. Also, in rural and suburban areas where septic tanks are used (o- and m-cresols can resist anaerobic digestion), human excrement may be a nonpoint source release of cresols to groundwater.

TABLE 5-1. Releases to the Environment from Facilities that Manufacture or Process Cresols[a]

Facility	Location	Total (lbs)						
		Air	Underground injection	Water	Land	Environment	POTW[b] transfer	Off-site transfer
Sloss Industries Corporation Coke Plant	Birmingham, AL	1,250	0	0	0	1,250	0	0
Chem-Four First, Ltd.	Demopolis, AL	0	0	0	0	0	0	250
Koppers Company, Inc.	Dolomite, AL	500	0	0	0	500	0	0
Empire Coke Company	Holt, AL	108	0	1	0	109	2	0
Merichem Company, Inc. (Black Warrior Plant)	Holt, AL	370	0	14	0	384	18,897	0
Ciba-Geigy Corporation	McIntosh, AL	500	0	250	250	1,000	0	0
CPS Chemical Company Of Arkansas	West Memphis, AR	0	0	1,200	0	1,200	0	23,000
Ansell Incorporated	Tucson, AZ	0	0	0	0	0	0	0
Basf Corporation Coatings and Inks Division	Anaheim, CA	310	0	0	0	310	0	0
FMC Corporation	Fresno, CA	33	0	0	0	33	0	0
Blue Coral Inc., McKay Chemical Div.	Los Angeles, CA	250	0	0	0	250	0	250
Tosco Corporation	Martinez, CA	500	0	250	250	1,000	0	0
FMC Specialties Group	Santa Fe Sprin, CA	3,240	0	0	0	3,240	3,240	0
		47,250	0	0	0	47,250	47,250	0
Mobil Oil Corporation Torrance Refinery	Torrance, CA	0	0	0	0	0	3,000	0
Uniroyal Chemical Company, Inc.	Naugatuck, CT	3,915	0	0	0	3,915	750	0
Texaco	Delaware City, DE	0	0	0	0	0	0	0
Wilmington Chemical Corporation	New Castle, DE	220	0	0	0	220	0	0
Harris Corporation Semiconductor	Palm Bay, FL	3,600	250	0	0	3,850	0	14,172
Westinghouse Electric Corporation	Athens, GA	500	0	0	0	500	0	750
Zep Manufacturing Company	Atlanta, GA	186	0	1	0	187	91	0
Amoco Performance Products Inc.	Augusta, GA	500	0	0	0	500	250	4,900
Amrep, Inc.	Cartersville, GA	5	0	0	0	5	1	0
G.E. Co., Medium Transformer Operation	Rome, GA	7,950	0	0	0	7,950	0	1,025
Acme Steel Company	Chicago, IL	500	0	0	0	500	250	0
PMC Specialties Group	Chicago, IL	8,966	0	0	0	8,966	13,752	0
PMC Specialties Group	Chicago, IL	2,975	0	0	0	2,975	2,349	0
		26,698	0	0	0	26,698	289,499	0
Koppers Company, Inc.	Cicero, IL	500	0	0	0	500	0	0
Spaulding Composites Specialty Plastics Div.	Dekalb, IL	500	0	0	0	500	0	500

TABLE 5-1 (Continued)

Facility	Location	Total (lbs)						
		Air	Underground injection	Water	Land	Environment	POTW[b] transfer	Off-site transfer
Chicago Magnet Wire Corp.	Elk Grove Village, IL	16,001	0	0	0	16,001	0	16,000
Borden, Inc. Chemical Division	Forest Park, IL	998	0	0	0	998	999	0
Reilly Tar and Chemical Corporation	Granite City, IL	1,000	0	0	0	1,000	250	342,168
Mobil Refining Corporation	Joliet, IL	250	0	250	0	500	0	0
Essex Group Inc.	Rockford, IL	0	0	0	0	0	0	8,317
Shell Oil Company	Roxana, IL	250	0	0	500	750	0	0
Essex Group Inc.	Fort Wayne, IN	29,000	0	0	0	29,000	250	19,800
Essex Inc., Chemical Processing Plant	Fort Wayne, IN	500	0	0	0	500	0	28,250
General Electric Company Motor Business	Fort Wayne, IN	51,901	0	0	0	51,901	0	16,513
Phelps Dodge Magnet Wire Co.	Fort Wayne, IN	28,250	0	0	0	28,250	0	81,400
Rea Magnet Wire Company, Inc.	Fort Wayne, IN	27,000	0	0	0	27,000	0	2,330
Citizens Gas and Coke Utility	Indianapolis, IN	208	0	0	0	208	0	3,154
Essex Group Inc.	Kendalville, IN	13,500	0	0	0	13,500	0	2,900
Rea Magnet Wire Co., Inc.	Lafayette, IN	71,000	0	0	0	71,000	0	23,000
New Haven Wire and Cable, Inc.	New Haven, IN	4,300	0	0	0	4,300	0	1,179
Essex Group Inc.	Vincennes, IN	16,050	0	0	750	16,800	o	1,202,950
Total Petroleum, Inc.	Arkansas City, KS	1	0	0	15	16	0	0
Texaco Ref. and Mktg., Inc.	El Dorado, KS	1,200	0	250	0	1,450	0	0
Koch Chemical Company	Pittsburg, KS	1,000	0	0	0	1,000	1,053	750
Phelps Dodge Magnet Wire Co.	Hopkinsville, KY	35,250	0	0	0	35,250	0	45,441
Borden, Inc. Chemical Division	Louisville, KY	998	0	0	0	998	0	0
		998	0	0	0	998	0	0
		998	0	0	0	998	0	0
Hi-Tek Polymers, Inc. Plant 2700	Louisville, KY	3	0	0	0	3	0	16
Exxon Refinery	Baton Rouge, LA	680	0	0	74	754	0	0
Exxon Chemical Americas Chemical Plant	Baton Rouge, LA	810	0	100	0	910	0	130
Hoechst Celanese Corporation	Baton Rouge, LA	3	0	2	0	5	0	0
Marathon Petroleum Company	Garyville, LA	0	0	250	250	500	0	0
Uniroyal Chemical Co., Inc.	Geismar, LA	445	0	0	0	445	0	0

TABLE 5-1 (Continued)

Facility	Location	Total (lbs)						
		Air	Underground injection	Water	Land	Environment	POTW[b] transfer	Off-site transfer
Citgo Petroleum Corporation	Lake Charles, LA	24,000	0	20	8	24,028	0	7
Du Pont Pontchartrain Works	Laplace, LA	162	0	0	0	162	0	0
Murphy Oil USA, Inc.	Meraux, LA	0	0	200	20	220	0	0
General Electric Company	Shreveport, LA	1,000	0	0	0	1,000	0	0
Conoco Lake Charles Refinery	Westlake, LA	500	0	250	0	750	0	0
PPG Industries, Inc.	Westlake, LA	0	0	0	0	0	0	0
Sippican, Inc.	Marion, MA	250	0	0	0	250	0	250
		250	0	0	0	250	0	250
Anderson Development Company	Adrian, MI	250	0	0	0	250	0	23,400
Allied-Signal, Inc.	Detroit, MI	1	0	0	0	1	9,960	990
Koch Refining Company	Saint Paul, MN	0	0	0	5	5	0	0
Dundee Cement Company	Clarksville, MO	2	0	0	0	2	0	0
Safety Kleen Corporation	Clarksville, MO	6	0	0	0	6	0	1
Westinghouse Electric Corporation	Jefferson City, MO	8,450	0	0	0	8,450	0	0
P. D. George Company	St. Louis, MO	500	0	0	0	500	250	1,000
Borg-Warner Chemicals, Inc. Baymar	Bay St. Louis, MS	6,945	0	0	0	6,945	0	0
Magneteck Universal Manufacturing	Mississippi, MS	8,180	0	0	0	8,180	0	750
Amerada Hess Corporation	Purvis, MS	0	0	0	0	0	0	240,000
Sandoz Chemicals Corporation Mt. Holly Plant	Charlotte, NC	500	0	250	250	1,000	0	0
General Electric Company Lighting Systems Dept.	Hendersonville, NC	3,450	0	0	0	3,450	0	0
General Electric Company Transformer Bus. Dept.	Hickory, NC	34,586	0	0	0	34,586	0	250
Rea Magnet Wire Company, Inc.	Laurinburg, NC	92,000	0	0	0	92,000	0	500
Southeastern Adhesives Company	Lenoir, NC	250	0	0	0	250	250	0
Radiator Specialty Co.	Matthews, NC	500	0	0	0	500	0	250
Thiele-Engdahl, Inc.	Winston-Salem, NC	64,621	0	0	0	64,621	0	3,000
Elektrisola Inc.	Boscawen, NH	58,840	0	0	0	58,840	0	5,803
Concord Chemical Co., Inc.	Camden, NJ	1,900	0	0	0	1,900	0	0
Henkel Corporation	Carlstadt, NJ	6,635	0	0	0	6,635	0	0
Givaudan Corporation	Clifton, NJ	500	0	0	0	500	250	0
Du Pont Chambers Works	Deepwater, NJ	0	0	0	12	12	0	0
FMC Specialties Group	Fords, NJ	1,000	0	0	0	1,000	250	14,604

TABLE 5-1 (Continued)

Facility	Location	Total (lbs)						
		Air	Underground injection	Water	Land	Environment	POTW[b] transfer	Off-site transfer
American Cyanamid Company Warners Plant	Linden, NJ	500	0	0	0	500	250	0
Union Carbide Corporation Bound Book Plant	Piscataway, NJ	448	0	0	0	448	0	0
		322	0	0	200	522	0	0
Ciba-Geigy Corporation	Toms River, NJ	182	0	455	0	637	0	27,838
Diaz Chemical Corporation	Holley, NY	0	0	0	0	0	250	12,570
BTL Specialty Resins Corp.	Niagara Falls, NY	500	0	0	0	500	0	0
		500	0	0	0	500	0	0
Occidental Chemical Corp. Durez Division	North Tonawanda, NY	0	0	6	0	6	0	0
General Electric Company Insulating Materials	Rotterdam, NY	2,000	0	0	0	2,000	0	25,000
Schenectady Chemicals, Inc.	Rotterdam Junction, NY	500	0	250	0	750	0	0
		500	0	250	0	750	0	0
		1,000	0	250	0	1,250	0	18,400
Schenectady Chemicals, Inc.	Schenectady, NY	1,000	0	0	0	1,000	0	0
		8,350	0	0	0	8,350	0	144,000
General Electric Plastics	Selkirk, NY	31,847	0	16	0	31,863	0	0
BASF Corporation Coatings and Inks Division	Cincinnati, OH	60	0	0	0	60	0	11,790
BASF Corporation Coatings and Inks Division	Cincinnati, OH	85	0	0	0	85	0	47,000
Hilton Davis Co.	Cincinnati, OH	500	0	0	250	750	750	0
Ashland Chemical Company	Cleveland, OH	500	0	0	0	500	0	6,431
Reilly Tar and Chemical Corporation	Cleveland, OH	1,000	0	0	0	1,000	250	42,160
General Electric Company Electromaterials Department	Coshocton, OH	5,450	0	0	0	5,450	0	0
Nordson Corporation-RBX Div.	Elyria, OH	500	0	0	0	500	0	3,800
Allied-Signal Inc.	Ironton, OH	5,740	0	250	20	6,010	0	2,000
New Boston Coke Corporation	New Boston, OH	5,373	0	0	0	5,373	0	0
Conoco Refinery	Ponca City, OK	1,000	0	250	250	1,500	0	0
Moore Business Forms and Systems Division	Stillwater, OK	0	0	0	0	0	0	250
Aristech Chemical Corporation Tarben Plant	Clairton, PA	118	0	0	0	118	0	18,107
		131	0	0	0	131	0	13,938
		170	0	0	0	170	0	15,979

TABLE 5-1 (Continued)

Facility	Location	Total (lbs)						
		Air	Underground injection	Water	Land	Environment	POTW[b] transfer	Off-site transfer
Westinghouse Electric Corporation	Manor, PA	3,250	0	0	0	3,250	0	0
Arco Chemical Company	Monaca, PA	0	0	0	0	0	0	0
Neville Synthese Organics Inc.	Oil City, PA	1,000	0	250	0	1,250	0	114,600
		3,350	0	0	0	3,350	0	0
		2,050	0	0	0	2,050	0	0
Rohm And Haas, Inc. Delaware Valley, Philadelphia	Philadelphia, PA	0	0	0	0	0	910	0
Pennzoil Products Company Rouseville Refinery	Rouseville, PA	500	0	250	0	750	0	0
Olin Hunt Specialty Products Inc.	Lincoln, RI	500	0	0	0	500	0	0
Hardwicke Chemical Co.	Elgin, SC	2,882	0	0	0	2,882	0	1,600
Westinghouse Electric Corporation	Hampton, SC	900	0	0	0	900	0	8,800
Essex Group Inc.	Franklin, TN	16,173	0	0	0	16,173	0	1,807
Doehler-Javis	Greeneville, TN	2,000	0	0	3,000	5,000	0	0
Mapco Petroleum, Inc.	Memphis, TN	0	0	0	0	0	20,600	0
W.m. Barr And Company, Inc.	Memphis, TN	0	0	0	0	0	250	0
Berryman Products, Inc.	Arlington, TX	250	0	0	0	250	0	0
Beaumont Refinery	Beaumont, TX	0	0	250	0	250	0	44,000
Neches River Treatment Corporation, Lower Neches	Beaumont, TX	0	0	220	0	220	0	3,500
Arco Chemical Company	Channelview, TX	30	0	0	0	30	0	2,480
The Goodyear Tire and Rubber Co.	Cheek, TX	750	0	250	5,200	6,200	0	0
Koch Refining Company	Corpus Christi, TX	3,900	0	0	830,000	833,900	0	130,000
Zep Manufacturing Company	De Soto, TX	119	0	0	0	119	0	0
W. J. Smith Wood Preserving Company	Denison, TX	1	0	0	0	1	10	0
		1	0	0	0	1	2	0
The Dow Chemical Company Texas Operations	Freeport, TX	158	0	8	0	166	0	0
Hill Petroleum Company	Houston, TX	500	0	250	0	750	0	1,250
Koppers Company, Inc.	Houston, TX	250	0	0	0	250	0	0
Merichem Company, Inc.	Houston, TX	8,772	1,295,095	5	0	1,303,872	0	17,315
Amrep, Inc.	Lancaster, TX	5	0	0	0	5	1	0
Reilly Tar and Chemical Corporation	Lone Star, TX	500	0	0	0	500	750	0
Crown Central Petroleum Corporation	Pasadena, TX	250	0	0	0	250	0	0

TABLE 5-1 (Continued)

Facility	Location	Total (lbs)						
		Air	Underground injection	Water	Land	Environment	POTW[b] transfer	Off-site transfer
Hoechst Celanese Corporation Bayport Works	Pasadena, TX	0	0	0	0	0	36	0
Sea Lion Chemical	Texas City, TX	250	0	0	0	250	0	44,950
		250	0	0	0	250	0	1,250
Sterling Chemicals, Inc.	Texas City, TX	750	0	0	0	750	250	0
Du Pont	Victoria, TX	360	96,000	0	11,200	107,560	0	0
Kennecott Utah Copper	Copperton, UT	250	0	250	250	750	0	0
Reilly Tar and Chemical Corporation (Ironton Plant)	Provo, UT	1,000	0	250	0	1,250	0	250
Westinghouse Electric Corp. Wire Division	Abingdon, VA	7,250	0	0	0	7,250	0	17,000
Northwest Petrochemical Corporation	Anacortes, WA	500	0	0	0	500	0	2,000
Mobil Oil Corporation	Ferndale, WA	0	0	250	500	750	0	0
Plastics Engineering Company	Sheboygan, WI	55	0	0	0	55	105	25
Koppers Company, Inc.	Follansbee, WV	758	0	0	0	758	0	0
Akzo Chemicals Inc.	Gallipolis Fer, WV	750	0	6,900	2	7,652	0	5,272
FMC Corporation	Nitro, WV	1,812	0	250	0	2,062	0	18,569

[a]Derived from TRI 1989.
[b]POTW = publicly-owned treatment works.

5. POTENTIAL FOR HUMAN EXPOSURE

Various plant lipid constituents contain cresols (Fiege and Bayer 1987). Runoff from terrestrial sources may contribute cresols to surface waters in addition to endogenous sources such as aquatic plants, animals, and microbes.

Cresols are natural components of crude oil and coal tar, from which they are recovered as fractional distillates. Cresols are also produced synthetically. The dominant anthropogenic sources for the release of cresols to water are fugitive or accidental discharges during the manufacture, use, transport, and storage of cresols or associated products of the coal tar and petroleum industries. Table 5-l includes information from the TRI (1989) on releases of cresols to water from facilities that process or manufacture cresols. However, the data do not separate groundwater releases from those made to surface waters. According to the TRI, 32 of 163 facilities that manufacture or process cresols released an estimated 14,400 pounds of this compound to water in 1987. The largest single annual discharge was 6,900 pounds, One hundred thirty-one facilities claimed that no cresol was released to water, while 7 sites discharged 20 pounds or less in 1987 (TRI 1989).

Low levels of cresols are constantly emitted in the exhaust from motor vehicle engines using petroleum-based fuels (Hampton et al. 1982; Johnson et al. 1989; Seizinger and Dimitriades 1972). Therefore, waterways used for transportation and recreation are likely to receive cresols from ship and motorboat traffic. Waste water effluents from coal gasification (Giabbai et al. 1985; Neufeld et al. 1985) and liquefaction facilities (Fedorak and Hrudey 1986), shale oil production sites (Dobson et al. 1985; Hawthorne and Sievers 1984), refineries (Cardwell et al. 1986; Snider and Manning 1982), and a poultry processing plant (Andelman et al. 1984) also may release cresols to surface waters.

In general, cresols will degrade in surface waters very rapidly. However, cresols may persist in groundwater due to a lack of microbes and/or anaerobic conditions. Cresols are largely released to groundwater via landfills and hazardous waste sites. Tables 5-2a through 5-2e include monitoring data for these sources.

Very little information regarding the release of individual isomers was located in the literature. A coal liquefaction waste water effluent contained o-cresol at a concentration of 586 mg/L (Fedorak and Hrudey 1986). o-Cresol was detected at an average concentration of 1.1 μg/L for three samples of retort water from a shale oil production facility (Hawthorne and Sievers 1984).

Waste water effluents from coal gasification facilities contained p-cresol at concentrations of 880 mg/L (Neufeld et al. 1985) and 5,120 ppb (Pellizzari et al. 1979). A coal liquefaction and a shale oil waste water effluent contained p-cresol at concentrations of 420 mg/L (Fedorak and Hrudey 1986) and 779 μg/L (Pellizzari et al. 1979), respectively. p-Cresol was

TABLE 5-2a. Detection of o-Cresol in the Groundwater of Hazardous Waste Sites and Landfills

Type/location	Sampling dates	Number of samples	Number positive	Concentration	Reference
Waste sites, groundwater					
Hazardous waste/ Buffalo, New York	No data	No data	No data	2.3 mg/L	Weber and Matsumoto 1987
Pine tar manufacturing/ Gainesville, Florida	No data	No data	No data	3.08 mg/L	Drinkwater et al. 1986
Wood preserving/ Pensacola, Florida	March 1984	19	6	0.04-7.10 mg/L	Goerlitz et al. 1985
Coal gasification/ Hoe Creek, Wyoming	No data	3	3	63-6,600 µg/L	Stuermer et al. 1982

TABLE 5-2b. Detection of p-Cresol in the Groundwater of Hazardous Waste Sites and Landfills

Type/location	Sampling dates	Number of samples	Number Positive	Concentration	Reference
Waste sites, groundwater					
Hazardous waste/ Buffalo, New York	No data	No data	No data	15 mg/L	Weber and Matsumoto 1987
Wood preserving/ Pensacola, Florida	March 1984	19	3	0.02-6.17 mg/L	Goerlitz et al. 1985
Landfill, groundwater					
Municipal/ Southington, Connecticut	1982-1983	No data	No data	1.5 mg/L	Sawhney and Kozloski 1984

TABLE 5-2c. Detection of m-Cresol in the Groundwater of Hazardous Waste Sites and Landfills

Type/location	Sampling dates	Number of samples	Number positive	Concentration	Reference
Waste sites, groundwater					
Wood preserving/ Pensacola, Florida	March 1984	19	4	0.05-13.73 mg/L	Goerlitz et al. 1985
Infiltration of wastewater, groundwater					
Municipal, secondary/ Fort Devens, Massachusetts	No data	2	1	0.02 µg/L	Bedient et al. 1984; Hutchins et al. 1980
Landfill, Groundwater					
Municipal/ Southington, Connecticut	1982-1983	No data	No data	0.6 mg/L	Sawhney and Kozloski 1984

TABLE 5-2d. Combined Detection of p- and m-Cresol in the Groundwater of Hazardous Waste Sites and Landfills

Type/location	Sampling dates	Number of samples	Number positive	Concentration	Reference
Waste sites, groundwater					
Pine tar, manufacturing/ Gainesville, Florida	No data	No data	No data	5.17 mg/L	Drinkwater et al. 1986
Coal gasification/ Hoe Creek, Wyoming	No data	3	3	9.6-16,000 µg/L	Stuermer et al. 1982

TABLE 5-2e. Detection of Unspecified Isomers of Cresol in the Groundwater of Hazardous Waste Sites and Landfills

Type/location	Sampling dates	Number of samples	Number positive	Concentration	Reference
Waste Sites, Groundwater					
Underground solvent storage tanks/ Santa Clara, California	March 1983	10	1	0.04 mg/L	Oliveira and Sitar 1985
Hazardous waste/ Coventry, Rhode Islan	1979-1984	4	1	0.114 mg/L	Ram et al. 1985

emitted with the waste water of a poultry processing plant at concentrations ranging from 2.14 to 22.5 µg/L (Andelman et al. 1984).

Waste water effluents from coal gasification facilities contained m-cresol at concentrations of 950 mg/L (Neufeld et al. 1985) and 2,670 µg/L (Pellizzari et al. 1979). A coal liquefaction and a shale-oil waste water effluent contained m-cresol at concentrations of 1,230 mg/L (Fedorak and Hrudey 1986) and 561 µg/L (Pellizzari et al. 1979), respectively.

Waste water effluents from coal gasification plants contained p- and m-cresol at a combined concentration of 1,840 mg/L (Giabbai et al. 1985). p- and m-Cresol were detected at a combined average concentration of 1.0 µg/L for three samples of retort water from a shale oil production facility (Hawthorne and Sievers 1984).

5.2.3 Soil

The dominant anthropogenic sources for the release of cresols to land are most likely spills during the manufacture, use, transport, and storage of cresols or associated products of the coal tar and petroleum industries. Table 5-l includes information from the TRI (1989) on releases of cresols to land from facilities that process or manufacture cresols. According to the TRI (1989), only 23 of 163 facilities that manufacture or process cresols released an estimated 853,256 pounds of this compound to land in 1987. The largest single annual discharge was 830,000 pounds. One-hundred forty facilities claimed that no cresol was released to land, while 5 sites discharged 20 pounds or less in 1987.

Cresols can enter soil from the same types of natural sources as described above. In fact, microbial activity may be an important contributor of cresols to soil. Poultry manure reportedly contained p-cresol at an average concentration of 11.7 mg/kg (Yasuhara 1987). Various plant lipid constituents contain cresols (Fiege and Bayer 1987). Consequently, natural cresols are constantly released to soils via excrement, exocellular secretions, and necromass of living and former living organisms, where they are expected to degrade rapidly (Section 5.3.2.3). Also, rural and suburban septic tanks and grazing animals on pasture lands may contribute large amounts of cresols to soil.

Cresols are released to soil at landfills and hazardous waste sites. In general, cresols will degrade in soil very rapidly. However, cresols may persist in soil under anaerobic conditions or due to the toxic effects of high concentrations of cresols or other associated compounds. Tables 5-2a through 5-2e include monitoring data for these sources. The land application of municipal sewage sludges that contain cresols may also release cresols to soil (Demirjian et al. 1984, 1987).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

The transport and partitioning of an organic compound in the environment is a function of the physical and chemical properties of that compound and the site-specific characteristics of the environment (e.g., percentage soil organic-matter). Based on the environmental correlations with physical properties (Lyman et al. 1982), the physical and chemical properties of the three isomeric cresols are sufficiently similar to indicate that similar transport and partitioning processes will be important for each isomer in the environment. Therefore, their potential for partitioning between the various environmental compartments will be discussed collectively.

In the atmosphere, the vapor pressure of the isomeric cresols, 0.11±0.30 mmHg at 25.5 °C (Chao et al. 1983; Daubert and Danner 1985), suggests that these compounds will exist predominantly in the vapor phase (Eisenreich et al. 1981). This is consistent with experimental studies that found all three isomers in the gas phase of urban air samples, but they were not present in the particulate samples collected at the same time (Cautreels and Vancauwenbergh 1978). The relatively high water solubility of the cresol isomers, 21,520-25,950 ppm (Yalkowsky et al. 1987), indicates that wet deposition may remove them from the atmosphere. This is confirmed by the detection of cresols in rainwater (Section 5.4.2). The short atmospheric residence time expected for the cresols (Section 5.3.2.1) suggests that cresols will not be transported long distances from their initial point of release.

Calculated soil adsorption coefficients (K_{oc}) of 17.5-117 have been determined for the three isomeric cresols, and compare favorably with experimentally determined values ranging from 22 to 158 (Boyd 1982; Koch and Nagel 1988). The estimated values were derived by regression analysis based on the inherent hydrophobicity (octanol/water partition coefficient [K_{ow}]) of an organic compound. For the soils studied in these adsorption studies, this type of regression analysis successfully predicted the potential for the movement of cresols through soil, suggesting high to very high mobility in soil (Swann et al. 1983).

The mobility of the isomeric cresols cannot be adequately described by considering their tendency to partition from water. The hydroxyl function of cresol is capable of forming relatively strong hydrogen bonds with active sites in the soil, and its mobility will depend on the degree in which these bonds are formed (Artiola-Fortuny and Fuller 1982; Boyd 1982; Southworth and Keller 1986). This was the rationale presented to explain large values obtained in laboratory experiments, which obtained K_{oc}, values for isomeric cresol ranging from 115 to 3,420 in a study of three different soils (Southworth and Keller 1986). A K_{oc}, value near 3,000 would suggest only slight mobility in soil (Swann et al. 1983). The amount of hydrogen bonding

to sites in the soil will be strongly influenced by the pH of the surrounding medium, the type of soil, its iron oxide content, anion exchange capacity, and the amount of organic matter present. From the literature, one cannot make generalized trends as to which soils provide active bonding sites for the cresol isomers. For example, m-cresol adsorbed strongly to a high-claycontent soil (Southworth and Keller 1986), but not to two others (Luh and Baker 1970).

In water, the isomeric cresols may eventually volatilize to the atmosphere, but volatilization is expected to be a slow process. Based on their Henry's law constants, which range from $1.2x10^{-6}$ to $8.65x10^{-7}$ atm-m^3/molecule (Gaffney et al. 1987; Hine and Mookerjee 1975), the volatilization half-life from a model river 1 m deep, flowing at 1 m/sec, with a wind velocity of 3 m/sec can be estimated to range from approximately 30 to 41 days (Lyman et al. 1982).

Experimental bioconcentration factors (BCFs) of 14.1 for o-cresol (Sabljic 1987) and 19.9 for m-cresol (Freitag et al. 1982) indicate that the isomers of cresol will not bioconcentrate in fish and aquatic organisms to any significant extent. Also, cresols are not likely to bioconcentrate in humans. Similar to their behavior in soil, the isomeric cresols are not expected to adsorb to sediment and suspended organic matter, although the potential for this process exists.

5.3.2 Transformation and Degradation

All cresol isomers can be rapidly removed from environmental media. The dominant removal mechanism in air appears to be oxidation by hydroxyl radical during the day and nitrate radical at night, with half-lives on the order of a day. In water under aerobic conditions, biodegradation will be the dominant removal mechanism; half-lives will be on the order of a day to a week. Under anaerobic conditions, biodegradation should still be important, but half-lives should be on the order of weeks to months. In soil under aerobic conditions, biodegradation is also important, but half-lives are less certain, although probably on the order of a week or less.

5.3.2.1 Air

Cresols degrade rapidly in air. Removal during the day is dominated by the reaction with hydroxyl radical (HO•), while nighttime removal is probably dominated by the nitrate radical. Reaction with other oxidants in air (e.g., ozone) will be much slower than reactions with hydroxyl or nitrate radical (Atkinson and Carter 1984).

Hydroxyl radicals react with cresols by attacking the carbon bearing the hydroxyl group. Degradation products from this reaction include nitrocresols and products of ring opening such as pyruvic acid, acetaldehyde, formaldehyde, peroxyacetylnitrate, and nitro-cresol (Atkinson et al. 1980; Grosjean 1984,

1985). Products may vary, depending on whether the reaction takes place in the gas or particle phase (Grosjean 1984). Atkinson (1985), after reviewing the kinetic data for hydroxyl radical reactions, determined the following second-order rate constants for o-, p-, and m-cresol: $4.0x10^{-11}$, $4.4x10^{-11}$, and $5.7x10^{-11}cm^3$ $molecule^{-1}$ sec^{-1}, respectively. He also stated that the estimated overall uncertainty in the rate constant for o-cresol was ±30%, while the estimated overall uncertainty for p- and m-cresol was ±35%. Using $5x10^5$ molecules cm^{-3} as an average tropospheric hydroxyl radical concentration (Atkinson 1985) and the reaction rate constants presented above, the atmospheric half-lives for o-, p-, and m-cresol were calculated to be 9.63, 8.75, and 6.76 hours, respectively. These values correspond to daylight hours when hydroxyl radicals are present.

At night, hydroxyl radical concentrations decrease and nitrate radical concentrations increase (Platt et al. 1984), making nitrate radical reactions more important than hydroxyl radical reactions. Nitrate radicals attack cresols by removing the hydroxyl hydrogen, yielding a phenoxy radical. The major reaction of this species is attack by the NO_2, radical to give products of nitration. Atkinson et al. (1984) and Carter et al. (1981) reported the reaction kinetics of nitrate radicals with cresol isomers. The reaction rate constants reported by these authors are similar and overlap when the uncertainties are considered. Averaged reaction second-order rate constants for the reaction between o-, p-, and m-cresol and the nitrate radical from data of Atkinson et al. (1984) and Carter et al. (1981) for the three isomers are $1.01x10^{-11}$, $0.70x10^{-11}$, and $1.08x10^{-11}cm^3$ $molecule^{-1}$ sec^{-1}, respectively. The half-lives for these reactions, assuming an average nitrate radical concentration of $2.4x10^8$, are 4.8, 4.5, and 6.9 minutes for o-, m-, and p-cresols, respectively (Atkinson et al. 1984; Carter et al. 1981). An order-of-magnitude decrease in the concentration of nitrate radicals yields half-lives of approximately 1 hour for all isomers. Under conditions of high nitrate concentrations, removal rates increase and half-lives decrease.

In addition to degradation by hydroxyl and nitrate radicals, all three cresol molecules absorb small amounts of uv light with wavelengths above 290 nm (Sadtler Index 1960a, 1960b, 1966). Therefore, direct photolysis is also possible; however, the photolysis rate is probably slow compared to the reaction with atmospheric radicals.

5.3.2.2 Water

Cresols have been tested for biodegradability in numerous screening tests and sewage treatment plant simulation tests, as well as in surface water, groundwater, and estuarine and sea water. Most tests indicate that the cresol isomers rapidly and completely degrade to simpler molecules under aerobic conditions in fresh water and that degradation is slower in salt water and under anaerobic conditions, although this is not always the case. m-Cresol gives more variable results in biodegradation tests than the other isomers. There are no hydrolyzable groups on cresol, so hydrolysis is not a

removal mechanism. Under some conditions, chemical oxidation may occur in water. Photolysis, especially in the presence of humic acid as a catalyst, may also be a significant removal mechanism.

All cresol isomers were found to degrade rapidly in biodegradation screening and sewage treatment plant,simulation studies with half-lives between less than 24 hours to less than 7 days (Alexander and Lustigman 1966; Babeu and Vaishnav 1987; Baird et al. 1974; Chambers et al. 1963; Heukelekian and Rand 1955; Ludzack and Ettinger 1960; Lund and Rodriguez 1984; Malaney 1960; Malaney and McKinney 1966; McKinney et al. 1956; Pauli and Franke 1971; Pitter 1976; Singer et al. 1979; Tabak et al. 1964; Young et al. 1968). In these studies, degradation was rapid with both acclimated and unacclimated inocula; initial concentrations ranged from 0.5 to greater than 500 ppm. Degradation generally was slower at the higher concentrations; however, under sewage treatment plant conditions, high cresol concentrations can be degraded (e.g., Chudoba et al. [1968] reported more than 99% removal of starting material (4,448 ppm of p-cresol) in 3 days under sewage treatment plant conditions). The available screening tests indicate that the cresols are readily degraded by microorganisms under sewage treatment plant conditions and in the environment, but no information about the degradation times in the environment can be inferred from screening study rate data..

Masunaga et al. (1983, 1986) reported the results of a study to determine the products of o-cresol degradation by activated sludge. o-Cresol was combined with phenol-acclimated activated sludge and samples, taken and analyzed by GC/MS over a 24-hour period. After less than 1.5 hours, o-cresol was not detected and hydroxylation products (dihydroxytoluenes) appeared, of which 3-methylcatechol seemed to be the major product. Catechols were subject to further hydroxylation reactions and ring opening reactions. While it is not known if the pathway used by a pure culture to metabolize a compound will be the same as that used by a mixed culture, similar pathways have been reported for p-cresol and m-cresol degradation with pure cultures isolated from industrial process effluents (Bayly and Wigmore 1973). These data suggest that the pathway of aerobic cresol degradation in sewage is similar to that reported for o-cresol.

In screening studies using digester sludge as the inoculum under anaerobic conditions, degradation is significantly slower than under aerobic conditions. o-Cresol yielded no detectable biodegradation in up to 98 days of incubation (Battersby and Wilson 1988, 1989; Boyd et al. 1983; Fedorak and Hrudey 1984; Horowitz et al. 1982; Shelton and Tiedje 1981; Wang et al. 1988, 1989) while p- and m-cresol showed extensive degradation under the same conditions in 20-98 days (Battersby and Wilson 1988, 1989; Boyd et al. 1983; Fedorak and Hrudey 1984, 1986; Fedorak et al. 1986; Horowitz et al. 1982; Roberts et al. 1987; Shelton and Tiedje 1981, 1984; Wang et al. 1988, 1989); however, p-cresol degrades more rapidly and with shorter acclimation times than m-cresol. o-Cresol also resists degradation in other anaerobic systems such as an anaerobic carbon filter (Suidan et al. 1981) and biofilms (Hu and

Shieh 1987), although some degradation is seen at low concentrations. m-Cresol also has shown resistance to anaerobic degradation under some conditions (Fedorak and Hrudey 1984). The degradation patterns of the cresol isomers appear to be the result of different degradation pathways for each isomer (Fedorak and Hrudey 1984, 1986; Fedorak et al. 1986; Roberts et al. 1987; Young and Rivera 1985). In general, the first reaction is hydroxylation of the methyl group on the aromatic ring, followed by oxidation to the hydroxy benzoic acid. Steric hindrance or electronic effects may make this a slow process for m-cresol and very-slow for o-cresol (Bossert and Young 1986; Suflita et al. 1989). These studies indicate that anaerobic degradation as a waste water treatment process for waste waters containing cresols will not be effective for removal, except for p-cresol. When used in combination with aerobic treatment, however, complete removal probably will occur.

Surface water grab samples are the best surrogates of natural behavior in aerobic environments, and rates determined in these systems are probably the closest to the rates seen in the environment. Research efforts studying the degradation of cresols in surface water grab samples generally have been directed at a better understanding of the kinetics involved in biodegradation. Of particular interest are the effects on biodegradation kinetics of substrate concentration (Hwang et al. 1989; Rogers et al. 1984; Spain and van Veld 1983), nutrient concentrations (Lewis et al. 1986; Shimp and Pfaender 1985a), spatial and temporal variations (including temperature variations) (Bartholomew and Pfaender 1983; Hwang et al. 1989; Palumbo et al. 1988; Visser et al. 1977), concentration of humic substances (Shimp and Pfaender 1985b), water source (and hence, bacterial population) (Paris et al. 1983; Rogers et al. 1984; Smith et al. 1978), and biofilms (Gantzer et al. 1988; Kollig et al .; Lewis et al. 1984, 1987). All of these factors affect the biodegradation kinetics, and no single equation has been formulated to consider their effects. First-order kinetics do not appear to describe adequately the biodegradation of cresols (Gantzer et al. 1988; Kollig et al. 1987; Lewis et al. 1984; Paris et al. 1983); rather, more complex relationships (e.g., Michaelis-Menten kinetics), and second-order kinetics (L organism^{-1} hour^{-1}) better describe the disappearance of cresols.

In general, second-order rate constants from diverse microbial communities are on the order of 10^{-9} to 10^{-10} L organism^{-1} hour^{-1} (Paris et al. 1983; Rogers et al. 1984; Smith et al. 1978), indicating that microbial populations capable of degrading cresols are ubiquitous in the environment and can degrade cresols at similar rates. Higher nutrient concentrations result in more rapid cresol degradation (Lewis et al. 1986; Shimp and Pfaender 1985a), while the presence of humic substances may slow degradation (Shimp and Pfaender 1985b). Cresol degradation is markedly slower at lower temperatures (Bartholomew and Pfaender 1983; Hwang et al. 1989) suggesting that, since metabolic rates slow down in winter, dilution may be a more important mechanism than biodegradation. In general, however, cresol isomers appear to degrade in natural waters rapidly with half-lives on the order of less than 1 hour to about 43 hours (Paris et al. 1983; Rogers et al. 1984; Smith et al.

1978; van Veld and Spain 1983). An adaptation period when no degradation occurs is sometimes important in natural microbial communities (Gantzer et al. 1988; Kollig et al. 1987; Lewis et al. 1984), but not always (Spain and van Veld 1983).

Very little information is available concerning the differences in the biodegradability of the cresol isomers. Based on the results of one study (Visser et al. 1977), biodegradability of their isomers appears to exist in the order: p-cresol > o-cresol > m-cresol. No confirmation of this order, however, could be found. In addition, aerobic degradation under these conditions appears to be fast, with the initial step being the rate-limiting step. No intermediate products have been reported using grab samples and the inoculum (Smith et al. 1978; Spain and van Veld 1983). Nonetheless, degradation probably proceeds along the same pathway described above for activated sludge.

In contrast to aerobic conditions, cresols do not appear to degrade rapidly in anaerobic freshwater sediments, although very little information is available. Horowitz et al. (1982) reported that the cresol isomers in anoxic sediments from Wintergreen Lake in Kalamazoo County, Michigan, had degradation times in excess of 29 weeks. The authors also stated that, as described above for anaerobic sludges, the m- and p-cresol isomers showed the most degradation, while o-cresol resisted degradation.

In anaerobic groundwater samples and groundwater samples with aquifer materials, cresol isomers display the same degradation pattern (i.e., p-cresol > m-cresol > o-cresol) seen in anaerobic sewage sludge experiments. However, aerobically incubated groundwater samples from anaerobic environments degrade all cresol isomers rapidly (Aelion et al. 1987; Arvin et al. 1988; Jensen et al. 1988; Swindoll et al. 1988). Smolenski and Suflita (1987) and Suflita et al. (1988) found that o-cresol under either sulfate-reducing or methanogenic conditions did not degrade when incubated with anoxic aquifer slurries. By contrast, p-cresol showed a lag time of less than 10 and 46 days under sulfate-reducing and methanogenic conditions, respectively, and m-cresol showed a lag time of 43 and 46-90 days under the same conditions. A more rapid degradation was seen after the lag time. Kuhn et al. (1988) also reported that o-cresol resisted degradation on anoxic columns filled with aquifer material and acclimated to m-xylene, while p- and m-cresol were degraded. Similar results were reported by Godsy et al. (1983) and Delfino and Miles (1985), while Thomas et al. (1989) reported that o-cresol concentrations decreased,

The degradation pathway of p-cresol in groundwater appears to proceed by oxidation of the methyl group to first give the corresponding benzaldehyde, then benroic acid (Kuhn et al. 1988; Smolenski and Suflita 1987; Suflita et

al. 1988, 1989). The hydroxybenzoic acid then can be either decarboxylated or dehydroxylated to phenol or benzoic acid, respectively.

Aerobic biodegradation in salt water (estuarine and sea water) appears to be slower than in fresh water; insufficient information is available to estimate anaerobic degradation in salt water. Factors similar to those discussed above have been studied with m- and p-cresol in salt water, including spatial and temporal variations (e.g., salinity and temperature) (Bartholomew and Pfaender 1983; Palumbo et al. 1988; Pfaender and Bartholomew 1982a, 1982b; Spain and van Veld 1983; van Veld and Spain 1983), substrate concentration (Palumbo et al. 1988; Spain and van Veld 1983), and the presence or absence of sediment (van Veld and Spain 1983). Almost no information is available for o-cresol, although one biological oxygen demand (BOD) test in saline water suggested rapid degradation (Takemoto et al. 1981).

In general, degradation decreases with increasing salinity, but probably not to an extent great enough to preclude biodegradation as a significant removal pathway (Palumbo et al. 1988). Under some conditions, acclimation appears to be significant (van Veld and Spain 1983), but this is not always the case (Spain and van Veld 1983). Degradation can be extremely sensitive to the location of the water sample used to conduct degradation tests. Variations were noted in water samples taken a few feet apart (Palumbo et al. 1988). The addition of sediments increases the degradation rate most of the time (van Veld and Spain 1983). Temperature, however, appears to be the most sensitive parameter studied (Bartholomew and Pfaender 1983; Palumbo et al. 1988; Pfaender and Bartholomew 1982a, 1982b). First-order kinetics do not fit biodegradation in saline water (Bartholomew and Pfaender 1983; Palumbo et al. 1988; Pfaender and Bartholomew 1982a, 1982b; van Veld and Spain 1983) and times to 50% disappearance are on the order of 15±50 hours or more.

p-Cresol has been reported to degrade under anaerobic conditions by microbes isolated from a salt marsh (Balba et al. 1982). but no kinetic data were presented.

In addition to biodegradation, chemical oxidation (including by superoxide, singlet oxygen, hydroxyl radical, and organic peroxy radicals) and photolysis may be removal pathways in the environment, but do not appear to be as fast as biodegradation under most conditions. Faust and Holgne (1987) reported that the irradiation of water containing fulvic acid produced a transient oxidant that oxidized o- and p-cresol. The transient radical was suggested to be an organic peroxy species. Irradiation of water without fulvic acid produced almost no degradation of p-cresol in 3 hours; the addition of fulvic acids caused rapid disappearance with half&times of about 50 minutes (Smith et al 1978). In water from Greifensee (a polluted, eutrophic, pre-alpine Swiss lake) at pH 8, calculated half-lives for the top meter of water (where light of the necessary wavelength is present) are 11 and 4.4 days for o- and p-cresol, respectively. Singlet oxygen is also produced by solar irradiation on natural waters and can react with cresols. A rate

constant of $3.7x10^{-8}$ M^{-1} sec^{-1} for p-cresol reaction with singlet oxygen was produced in the laboratory by irradiation of water containing rose bengal (Scully and Hoigne 1987). Using a singlet oxygen concentration of $4x10^{-14}$ M (corresponding to the concentration in water at noon on a summer day), these authors calculated a half-life of 500 hours. Smith et al. (1978) studied the direct photolysis of p-cresol in water. In pure water and using solar irradiation in April, Smith et al. (1978) reported half-lives of approximately 35 days.

While the above data indicate that oxidative and photolytic processes occur during degradation of cresols in water, it is difficult to estimate the half-lives for these under environmental conditions. Since environmental waters vary significantly in clarity (and hence, in their ability to transmit light), as well as their concentration of fulvic substances, half-lives are expected to vary considerably. Additionally, the absorbance of cresols changes with the pH of the water (Smith et al. 1978). Thus, the amount of light absorbed by cresols will change with pH as will the degradation rates. Smith et al. (1978) estimated a half-life of p-cresol in environmental waters from direct photolysis of 300-400 days under summer light conditions. This and the other estimates presented above suggest that chemical oxidation from light-produced radicals and direct photolysis will not be a significant removal mechanism under most environmental conditions.

In addition to oxidants generated by light, Stone (1987) reported that ferrous iron [Fe(III)] and manganese [Mn(III/IV)] oxides are capable of oxidizing p-cresol. Fe(III) and Mn(III/IV) oxides are common species found in surface water particulate and soils, as well as in dust and ash. Rate constants for p-cresol ranged from 10^{-9} to $l0^{-6}$ M^{-1} min^{-1} for pH of 7.8-4.2, respectively. In the environment and at low pH values, these species may oxidize cresols with half-lives on the order of several hours. The exact concentration of Fe(II1) and Mn(III/IV) oxides in environmental media and their availability for reaction, however, are not clear; therefore, the roles of these species in the degradation of cresols in the environment are difficult to determine.

5.3.2.3 Soil

Cresol degradation in soil has been reported by Medvedev and Davidov (1981a, 1981b), Namkoong et al. (1988), and Dobbins and Pfaender (1988). Dobbins and Pfaender (1988) and Namkoong et al. (1988) found that the data for cresol degradation fit first-order kinetics but with very different rates. Dobbins and Pfaender (1988) found that CO_2 from m-cresol degradation evolved slowly when m-cresol was incubated in water slurries of surface and subsurface soils from a pristine location. Degradation was followed by trapping radioactive carbon dioxide, and overall mass balances were performed by comparing radioactivity remaining in the soil with the trapped CO_2 In surface soils, first-order rate constants based on CO_2 evolution were

$7.55x10^{-5}$ - $6.31x10^{-4}$ $hour^{-1,}$ which yields half-lives from 46 days to about 1 year.

By contrast, Namkoong et al. (1988) reported a rapid degradation of all cresol isomers in surface soils from an uncultivated grassland site. Degradation was followed by analyzing for the parent substance, and first-order kinetics were followed. o-Cresol reportedly had a half-life of about 1.6 days, while p-cresol degraded too fast to allow measurement of a rate constant. m-Cresol reportedly had a half-life of about 0.6 days. Medvedev and Davidov (1981a, 1981b) reported the same relative rates for the three isomers in a soil from the Soviet Union but did not report absolute rates. Times to disappearance in the soil were reportedly 16, 9, and 27 days for o-cresol, p-cresol, and m-cresol, respectively. These authors were unable to detect any secondary products from cresol metabolism. The differences in the rates reported by Namkoong et al. (1988) and Dobbins and Pfaender (1988) appear to be the result of the different analytical methods used. Namkoong et al. (1988) used gas chromatography to determine the rate of cresol disappearance, while Dobbins and Pfaender (1988) used CO_2 evolution to determine the rate of carbon dioxide appearance. Thus, based on the available information, cresols degrade rapidly in soils, possibly becoming incorporated into soil microorganisms, but they mineralize slowly. Indeed, Dobbins and Pfaender (1988) noted that significant amounts of radioactivity were bound to the soil, which supports the explanation that cresols are incorporated.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Monitoring data have not shown cresols to be widely occurring atmospheric pollutants. The National Ambient Volatile Organic Compounds (VOCs) Database, a compilation of published and unpublished air monitoring data from 1970 to 1987, contained very little information on the cresols (Shah and Heyerdahl 1989). The database contained only information for o-cresol in source-dominated atmospheres (air surrounding a facility or known release of the chemical in question). The-median air concentration of o-cresol at source-dominated sites is 0.359 ppb for 32 samples (Shah and Heyerdahl 1989).

Cresol was detected in the ambient air of Upland, California; however, specific isomers were not identified (Kolber et al. 1981).

The absence of data does not necessarily indicate a lack of cresol emissions into ambient air. In general, cresols are highly reactive with hydroxyl and nitrate radicals in the day and night, respectively, and atmospheric half-lives for cresols are short. Scavenging by water may further reduce the atmospheric residence time of cresols (see Section 5.3.2.1).

5.4.2 Water

Information pertaining to the occurrence of cresols in surface waters was limited. STORET (1989) and the CLPSD (1988) contained no records for o-cresol in ambient surface water. o-Cresol was detected in freshwater samples from Spirit Lake, Washington, on August 7, 1980 and from South Fork Castle Lake and Smith Creek, Washington, on September 11, 1980 at unreported concentrations (McKnight et al. 1982). The presence of cresols was attributed to the Mount St. Helens eruption on May 18, 1980 (Mcknight et al. 1982). Whether or not the cresols originated from wood fires or the actual eruption was not clarified.

According to STORET (1989), the minimum, maximum, mean, and median p-cresol concentrations for 8 unremarked ambient surface water data points (those data points that are not noted to be less than a given value, usually the detection limit) are 10.0, 77.0, 39.1, and 29.0 μg/L. p-Cresol was detected in surface water with a frequency of occurrence of 1.5% and with a geometric mean concentration of 11 ppb for positive samples (CLPSD 1988). p-Cresol was identified as a contaminant of mixed water and sediment samples from the Tennessee River (Gordon and Goodley 1971) at a concentration of 200 μg/L (Goodley and Gordon 1976). p-Cresol also was detected in freshwater samples from Spirit Lake, Washington, on August 7, 1980 at unreported concentrations (McKnight et al. 1982).

The minimum, maximum, mean, and median m-cresol concentrations for 2 unremarked ambient surface water data points are 16.0, 23.0, 19.5, and 16.0 μg/L (STORET 1989). m-Cresol was detected with a frequency of occurrence of 0.9% in surface water (CLPSD 1988). In addition, m-cresol was listed as a contaminant of the St. Joseph River in the Lake Michigan Basin (Great Lakes Water Quality Board 1983). m-Cresol was detected in freshwater samples from Spirit Lake, Washington, on August 7, 1980 at unreported concentrations (McKnight et al. 1982).

The mean and median concentration of mixed cresols for 1 unremarked ambient surface water data point is 29.0 μg/L (STORET 1989). Information on mixtures of cresols was not included by the CLPSD (CLPSD 1988). Likewise, unspecified isomers of cresol were detected from 1 of 7 sample sites along the Delaware River at a concentration of 20 ppb. This was a result of industrial waste water effluent discharged by the Philadelphia Northeast Sewage Treatment Plant, which discharges secondary effluent into the river (Hites 1979; Sheldon and Hites 1979). For Delaware River water from August 1976 to March 1977, the summer and winter average concentrations of unspecified isomers of cresols that were not traceable to any source were "not detected" and 2 ppb, respectively; this suggested that rapid biodegradation prevents cresol detection during the warmer months (Sheldon and Hites 1978).

Again, the absence of monitoring data does not necessarily indicate a lack of cresols in the environment. Cresols are widely occurring natural and

anthropogenic products. However, biodegradation is probably the dominant mechanism responsible for the rapid removal of cresols from surface waters (see Section 5.3.2.2). Nevertheless, cresols may persist in extremely oligotrophic waters, in waters with limited microbial communities, and/or under anaerobic conditions such as in some sediments and groundwater aquifers.

Tables 5-2a through 5-2e summarize the literature data on cresols found in groundwater and their respective anthropogenic sources. STORET (1989) did not contain records for o-cresol in groundwater.

The minimum, maximum, mean, and median p-cresol concentrations for 3 unremarked groundwater data points are 10.0, 4,000.0, 1,364.0, and 82.0 μg/L (STORET 1989).

The minimum, maximum, mean, and median m-cresol concentrations for 104 unremarked groundwater data points are 0.0, l00,000.0, 9,713.0, and 7.0 μg/L (STORET 1989).

The minimum, maximum, mean, and median concentrations of mixed cresols for three unremarked groundwater data points are all 5.0 μg/L (STORET 1989).

Only two reports were found in the literature that quantified cresols in precipitation. Rainwater at Portland, Oregon, contained o-cresol at concentrations ranging from 240 to 2,800 ng/L, with an average concentration of 1,020 ng/L for 7 rainfalls between February 12, 1984 and April 12, 1984. Combined p- and m-cresol concentrations ranged from 380 to 2,000 ng/L, with an average concentration of greater than 1,100 ng/L (Leuenberger et al. 1985a). o-Cresol was detected in rainwater from a rural site (Grepden, Switzerland) on April 3, 1986, at concentrations ranging from not detected to 1.3 μg/L. Combined p- and m-cresol concentrations ranged from 0.65 to 9.3 μg/L (Czuczwa et al. 1987).

5.4.3 Soil

Monitoring data pertaining to cresols found in soil were not found in the literature. Nonetheless, o-cresol was detected in 3.7% of the soil samples in the CLPSD (CLPSD 1988).

For the CLPSD, p- and m-cresol were detected with frequencies of occurrence of 4.4% and 0.9%, and with geometric mean concentrations of 257 and 1,105 ppb for the positive samples, respectively. Information on mixtures of cresols was not included by the CLPSD (CLPSD 1988).

Cresols are an excretory product of mammals and an intermediate biotransformation product of natural aromatics such as lignin constituents (Fiege and Bayer 1987). Consequently, soil microorganisms are capable of metabolizing cresols, and any anthropogenic release of cresol, other than massive spills, is likely to be rapidly degraded in soil (Section 5.3.2.3).

5.4.4 Other Environmental Media

As discussed above, cresols are widely distributed natural compounds. They are formed as metabolites of microbial activity and are excreted in the urine of mammals. Various plant lipid constituents, including many oils, contain cresols. Cresols have also been detected in certain foods and beverages such as tomatoes, tomato ketchup, cooked asparagus, various cheeses, butter, oil, red wine, distilled spirits, raw and roasted coffee, black tea, smoked foods, tobacco, and tobacco smoke (Fiege and Bayer 1987). However, very few monitoring data for cresols in food were found in the literature.

All three cresol isomers were identified as volatile emissions of fried bacon (Ho et al. 1983). Various brands of Scotch whiskey, whiskeys made outside of Scotland, cognac, armagnac, brandy other than cognac and armagnac, and white and dark rums contained cresol at concentrations ranging from 0.01 to 0.20 ppm, 0.01 to 0.07 ppm, trace to 0.02 ppm, trace to 0.02 ppm, trace to 0.02 ppm, and trace to 0.20 ppm, respectively (Lehtonen 1983).

Cresols are emitted in cigarette smoke; the total concentration of all three isomers is about 7.5 μg per cigarette (Wynder and Hoffman 1967). An individual who smokes two packs of cigarettes a day may inhale approximately 3.0 μg/day.

5.5 GENEPAL POPULATION AND OCCUPATIONAL EXPOSURE

Cresols have been identified as components of automobile exhaust (Hampton et al. 1982; Johnson et al. 1989; Seizinger and Dimitriades 1972), and may volatilize from gasoline and diesel fuels used to power motor vehicles. Vehicular traffic in urban and suburban settings provides a constant source of cresols to the atmosphere. Hence, urban and suburban populations may be constantly exposed to atmospheric cresols. Cresols are also emitted to ambient air during the combustion of coal (Junk and Ford 1980), wood (Hawthorne et al. 1988, 1989), municipal solid waste (James et al. 1984; Junk and Ford 1980), and cigarettes (Arrendale et al. 1982; Novotny et al. 1982). Therefore, residents near coal- and petroleum-fueled electricity generating facilities, municipal solid waste incinerators, and industries with conventional furnace operations or large-scale incinerators may be exposed to cresols in air. People in residential areas where homes are heated with coal, oil, or wood may also be exposed to cresols in air.

Exposure to cresol may occur in atmospheres containing toluene. Cresols are formed in the atmosphere during photochemical reactions between toluene and photochemically generated hydroxy radicals (Leone et al. 1985).

The most common route of exposure for the general population is probably inhalation. However, cresols have a short residence time in both day- and night-time air; despite continual releases of cresols to the atmosphere, levels are probably low. Very few atmospheric monitoring data are available

in the literature; therefore, an average daily intake via inhalation was not calculated. Cigarette smoke is also a source of atmospheric exposure. An individual who smokes two packs of cigarettes a day may inhale 3.0 μg/day (Wynder and Hoffman 1967).

Ingestion of certain foods may be as or more prevalent a route of exposure than inhalation. However, more quantitative data on the occurrence of cresols in food would be required to make a comparison. Cresols have been detected in tomatoes and tomato ketchup, cooked asparagus, various cheeses, butter, and oil (Fiege and Bayer 1987). Beverages such as red wine and distilled spirits (Lehtonen 1983), raw and roasted coffee, and black tea contain cresols (Fiege and Bayer 1987). Fried (Ho et al. 1983), smoked, and barbecued foods also may contain cresols (Fiege and Bayer 1987). For people with groundwater wells near landfills or hazardous waste sites, drinking water may be an important source of exposure, as well as the air for individuals living near hazardous waste sites or cresol production facilities. Quantitative information for both foods and drinking water was lacking, and the respective average daily intakes were not calculated.

Dermal contact to cresols may occur during recreational activities at natural waterways containing either naturally or anthropogenically generated cresols. However, cresols are expected to degrade rapidly in surface water.

An estimated 21,156, 33,257, 11,162, and 1,261,818 workers were potentially exposed to o-, p-, m-, and the mixture of isomers, respectively, in the workplace, according to the National Occupational Hazard Survey (NOHS) conducted between 1972 and 1974 (NIOSH 1984). According to the National Occupational Exposure Survey (NOES) conducted by NIOSH in the workplace between 1980 and 1983, 3,214, 3,269, 5,573, and 121,573 workers were potentially exposed to o-, p-, m-, and the mixture of isomers, respectively (NIOSH 1989). Neither the NOHS nor NOES data bases contain information on the frequency, concentration, or duration of exposure of workers to any of the chemicals listed therein. These surveys provide estimates of the number of workers potentially exposed to the chemicals in the workplace. The most probable routes of occupational exposure are inhalation and dermal contact at places where cresols and/or cresol-containing compounds are produced or used.

Very little information pertaining to occupational exposure to cresols was located in the literature. Occupational exposure to cresol has been documented in laboratories and coal gasification facilities (Needham et al. 1984), during paint and varnish application (Angerer and Wulf 1985), during application of insulation lacquers to copper wires, and in wood-preserving facilities (Nieminen and Heikkila 1986). During the creosote impregnation of wood, workers were exposed to cresol concentrations less than 0.1 mg/m^3 (Heikkila et al. 1987). Workers of a bench scale coal conversion process were exposed to atmospheric levels of cresols less than 0.1 ppm in 1981 and 1982 (Dreibelbis et al. 1985).

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

High levels of exposure to cresols are most likely to occur in occupational settings where cresols are either produced or used. Intake by inhalation or dermal contact is the most probable route of high exposure to cresols. Cigarette smokers may be exposed to high amounts of cresols.

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA as amended directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of cresols is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of cresols.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that, if met, would reduce or eliminate the uncertainties of human health assessment. In the future, the above data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed,

5.7.1 Data Needs

Physical and Chemical Properties. The physical and chemical properties necessary to estimate the fate and transport of cresols in the environment have been described for all isomers (Amoore and Hautula 1983; Artiola-Fortuny and Fuller 1982; Boyd 1982; Chao et al. et al. 1985; Gaffney et al. 1983; Daubert and Danner 1985; Freitag 1987; Hansch and Leo 1985; Hine and Mookerjee 1975; OHM/TADS 1989; Riddick et al. 1986; Sax and Lewis 1987; Verschueren 1983; Weast et al. 1988; Windholz et al. 1983; Yalkowsky et al. 1987). Knowledge of some of these properties was required to describe the fate and transport of cresols because adequate experimental data were not available. The database was sufficient to perform the necessary estimates (Lyman et al. 1982).

Production, Import/Export, Use, and Disposal. Current production volumes are available (USITC 1989), as are historical and predictive production volume information (CMR 1987; USITC 1986). Information on the uses of cresols is available including the use as a chemical intermediate and wood preservative. Information on the release of cresols to the environment (Andelman et al. 1984; Arrendale et al. 1982; Cardwell et a1.1986; Dobson et al. 1985; Fedorak and Hrudey 1986: Giabbai et al. 1985; Hampton et al. 1982;

Hawthorne and Sievers 1984; Hawthorne et al. 1988, 1989; James et al. 1984; Johnson et al. 1989; Junk and Ford 1980; Leone et al. 1985; Liberti et al. 1983; Neufeld et al. 1985; Novotny et al. 1982; Pellizzari et al. 1979; Seizinger and Dimitriades 1972; Snider and Manning 1982) from manufacturing, production, and use (TRI 1989) and to the workplace, as well as their presence in foods and other natural sources, is available (Fiege and Bayer 1987; McKnight et al. 1982; Needham et al. 1984). Disposal methods are also well described. Information concerning the number of persons potentially exposed to cresols near waste sites and manufacturing, production, and use facilities, however, is not available. High production and widespread use make the potential for human exposure high.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxic Release Inventory, which contains this information for 1987, became available in May of 1989. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. Information concerning the partitioning of cresols in the environment is available; cresols occur in all environmental media. Information on the transport of cresols in environmental media is also available; however, the confounding influence of pH on soil transport makes assessing soil leaching difficult. An extensive data base is available describing the aerobic (rapid) (Alexander and Lustigman 1966; Babeu and Vaishnav 1987; Baird et al. 1974; Chambers et al. 1963; Heukelekian and Rand 1955; Ludzack and Ettinger 1960; Lund and Rodriguez 1984; Malaney 1960; Malaney and McKinney 1966; McKinney et al. 1956; Pauli and Franke 1971; Pitter 1976; Singer et al. 1979; Tabak et al. 1964; Young et al. 1968) and anaerobic (slow) (Battersby and Wilson 1988, 1989; Boyd et al. 1983; Fedorak and Hrudey 1984; Horowitz et al. 1982; Shelton and Tiedje 1981; Wang et al. 1988, 1989) degradation of cresols in water and appears to be consistent; however, soil biodegradation data are few and conflicting. The atmospheric fate of cresol isomers is well described and suggests that cresols are rapidly degraded in air (Atkinson 1985; Atkinson et al. 1980; 1984; Carter et al. 1981; Grosjean 1984, 1985; Platt et al. 1984).

Bioavailability from Environmental Media. Case reports of people who have experienced cresol poisoning following oral and dermal exposure indicate that all cresols can be absorbed by these routes (Cason 1959; Chan et al. 1971; Green 1975). However, no information is available regarding oral or dermal absorption of cresols located in water, soil, or plant material. Studies in animals have shown that cresols can be absorbed from contaminated air by inhalation but have not attempted to quantify this absorption. Studies of absorption of cresols from air, water, soil, and plant material would allow determination of the rate and extent of absorption from each of these media and comparison of the potential hazard posed by cresols contained in each.

Food Chain Bioaccumulation. Few data are available describing the food chain bioaccumulation of cresols. The available experimental data (Freitag et al. 1985) are consistent with estimated values obtained from regression equations which suggest that it will not bioconcentrate to any significant extent (Lyman et al. 1982). Information concerning the potential for biomagnification has not been described, although the log K_{ow} values are small and biomagnification is expected to be insignificant.

Exposure Levels in Environmental Media. Information on exposure levels in environmental media is available for groundwater (Bendient et al. 1984; Drinkwater et al. 1986; Goerlitz et al. 1985; Hutchins et al. 1980; Oliveira and Sitar 1985; Ram et al. 1985; Sawhney and Kozlowski 1984; Stuermer et al. 1982; Weber and Matsumota 1987) only (sources of groundwater contamination include hazardous waste sites). Data describing the exposure levels in air and surface water are lacking. It is not clear whether monitoring studies were not performed, or were not found. Quantified levels of cresols in food are also lacking. Estimates of human intake are not available.

Exposure Levels in Humans. Cresols are naturally occurring substances that are present in human urine (Fiege and Bayer 1987), and data on this are available. Cresols may also be present as a result of the metabolic breakdown of other organic compounds, such as toluene (Needham et al. 1984). As such, positive monitoring for cresols in humans does not necessarily mean exposure to them. The ability to rigorously establish cresol exposure levels in humans has yet to be demonstrated.

Exposure Registries. No exposure registries for cresols were located. This compound is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The compound will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to the exposure to this compound.

5.7.2 On-going Studies

For o-, p-, and m-cresol, as well as the mixed isomers, anaerobic degradation studies, analytical methods development, and transformation studies are all on-going (EPA 1989b). Additionally, for o-cresol, studies on water purification techniques are on-going, while for p-cresol, aerobic degradation and toxicity studies are on-going.

As part of the Third National Health and Nutrition Evaluation Survey (NHANES III), the Environmental Health Laboratory Sciences Division of the

5. POTENTIAL FOR HUMAN EXPOSURE

Center for Environmental Health and Injury Control, Centers for Disease Control, will be analyzing human urine samples for cresols and other phenolic compounds. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population.